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Towards a Catalyst for Alkene Hydroamination – Static and Dynamic *Ab Initio* DFT Studies

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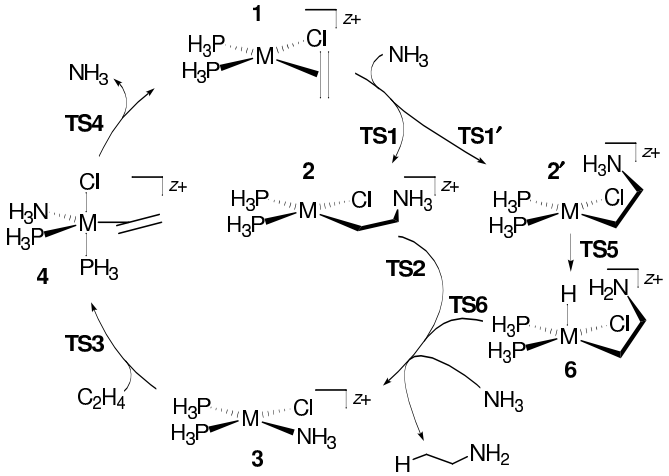
Using density functional theory, we have investigated group 9 and group 10 d^8 transition-metal complexes in view of their potential application as catalysts for the **hydroamination of alkenes** [1]. We used the **projector-augmented wave (PAW) method** [2], a plane-waves-based method with all-electron wavefunctions capable of performing **Car–Parrinello *ab initio* molecular dynamics** simulations.

Transition states were located using friction dynamics combined with a moving constraint to drive the system over the barrier, while all other degrees of freedom were being relaxed. Dynamical reaction paths were obtained by letting the system evolve freely from the transition state, thus allowing a detailed analysis of the time evolution of the reaction event [3].

The principal mechanistic pathway explored involves external nucleophilic attack of the amine on the coordinated alkene (C=C activation), followed by either protonolytic cleavage of the metal–alkyl bond or protonation of the metal with subsequent C–H reductive elimination. Complexes of the type $\{MCl(PH_3)_2\}^{n+}$ have been studied, where M = Ni(II), Pd(II), Pt(II) (n = 1) or M = Co(I), Rh(I), Ir(I) (n = 0).

The reaction profiles for the complete catalytic cycle will be discussed, assessing the suitability of the metal complexes. The influence of ligand electronic effects on the rate-determining step has been investigated by replacing PH_3 by a series of substituted phosphanes PR_3 (R = F, CF_3, Me, NMe_2, Ph, *p*-C_6H_4OMe, *p*-$C_6H_4NMe_2$) with different electron-donating capabilities.



[1] For a recent review, see: T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–703.

[2] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.

[3] P. E. Blöchl, H. M. Senn, A. Togni, in *Transition State Modeling for Catalysis*, D. G. Truhlar, K. Morokuma, Eds., ACS Symposium Series 721, American Chemical Society, Washington, DC, 1999, pp. 88–99.